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REMARKS

Applicant has amended the specification by adding appropriate subject matter from U.S. Provisional Application Nos. U.S.S.N. 60/117,852 and 60/117,854 to page 6 of this application. Given that this information was previously incorporated by reference, no new matter has been added.

The Examiner should note that a related application – U.S.S.N. 10/436,944, which claims priority to the '852 provisional application, has been published as U.S. Pat. Pub. No. 2003-0201223 A1. A search of the PTO "PAIR" database for U.S.S.N. 60/117,852 leads to this published application.

Claims 19, 20, and 22 are rejected under 35 U.S.C. §102(b) as being clearly anticipated by, or in the alternative, under 35 U.S.C. §103(a) as obvious over EP 0299459 A2. These rejections are respectfully traversed for the following reasons:

EP 0299459 teaches away from the inventions defined by claims 19, 20 and 22, which include now the express limitations that (1) the potting materials and the hollow fiber membranes are made from different thermoplastic, perfluorinated resins, and (2) the potting materials melt at a temperature below the melting point of the hollow fiber membranes. As taught in the EP Patent:

> The powdery thermoplastic resin is a resin which may be the same as or different from the resin used for the hollow fiber filter membranes and which is compatible with the resin used for the membranes and has a softening point preferably 0.5 to 1.5 times, more preferably 0.8 to 1.2 times, as high as the softening point (DEG C) of the thermoplastic resin used for the hollow fiber filter membranes. ***It is preferred that the powdery thermoplastic resin have the same softening point as that of the resin used for the membranes. It is most preferred that***

the powdery thermoplastic resin be of the same type as the resin used for the membranes.

In the rejected claims, the thermoplastic potting resin must be different from the thermoplastic resin used to form the hollow fiber membranes. In addition, the melting point of the potting material must be below the melting point of the hollow fiber filter membranes. In the EP Patent, this is not true – the materials (and/or the melting points) can be the same. The resulting potted bundles of thermoplastic hollow fiber filter membranes are thus neither the same nor obvious variants of one another. This Section 102/103 rejection of claims 19, 20 and 22 should be withdrawn. Such action is respectfully requested.

Claims 20, and 22 are rejected under 35 U.S.C. §102(b) as being clearly anticipated by, or in the alternative, under 35 U.S.C. §103(a) as obvious over Niermeyer (US 5,695,702). These rejections are respectfully traversed for the following reasons:

In the rejected claims, the thermoplastic potting resin must be different from the thermoplastic resin used to form the hollow fiber membranes. Niermeyer teaches a thermoplastic fluoropolymer for the potting material (in claim 8) and teaches the use of PTFE for the hollow fibers (in Claim 10). However, PTFE is not a thermoplastic fluoropolymer, as shown below from a dictionary definition of the two terms:

> **TFE (Polytetrafluoroethylene)**
> A high temperature fluoropolymer used as cable insulation. Because it is not melt processable, it is applied as a paste extrusion and then sintered or used in tape form. Also called PTFE.
>
> **Thermoplastic** - A classification of material that can be readily softened and reformed by heating and be rehardened by cooling.

Accordingly, this Section 102/103 rejection of claims 20 and 22 should be withdrawn. Such action is respectfully requested.

Claims 1-18, 21, and 23 are rejected under 35 U.S.C. §103(a) as being unpatentable over Huang et al (US 5,284,584) in view of EP 0299459 A2 and Miyagi et al (US 5,114,508). These rejections are respectfully traversed for the following reasons:

Claim 1 has been replaced with new Claim 28. Huang neither teaches nor suggests the method recited in new Claim 28. Huang claims a method of fabricating a spiral-type hollow fiber membrane fabric-containing cartridge, comprising the following steps:

a. forming a plurality of hollow fiber membranes each having a lumen, into a fabric-like array having a warp and a weft, in which the hollow fibers substantially are mutually-parallel and constitute the fabric weft, and are held in spaced-apart relationship by filaments constituting the fabric warp; then

b. winding the array upon an axis which is substantially parallel to the hollow fibers into a spirally-wound membrane bundle having two bundle ends and a cylindrical exterior surface; and

c. simultaneously with step (b.), extruding in molten form a high-strength, solvent resistant thermoplastic resin having a melting point at least about 10°C below the melting point of the hollow fibers, and having a melt flow index between about 0.01 to about 150 grams/10 minutes; and directing said resin onto each of the two bundle ends to thereby pot each of the two bundle ends in said resin, serving to seal the bundle end into an adjacent monolithic tube sheet, a portion of the bundle between the two tube sheets being free from resin to form a shell-side region; and then

d. exposing the lumen ends of the hollow fibers constituting at least a first one of the bundle ends to communicate with the exterior of the bundle.

According to Huang, preferably, the hollow fibers are made from a thermoplastic resin. More preferably, they are made from the same thermoplastic resin as is selected as the solvent resistant thermoplastic resin for potting the hollow fiber membrane fabric. Most preferably, the hollow fibers are made from polyolefins. The tube sheets must be fabricated from a high-strength, solvent resistant thermoplastic resin, and the resin must be extruded at an elevated temperature to form a molten band of potting material that is directed onto the surface of the hollow fiber membrane fabric to be potted. In preferred embodiments, the solvent resistant thermoplastic resin is a polyolefin resin. The other components of the cartridges and modules can be fabricated from any suitable conventionally-known materials. Preferably, such other components themselves also demonstrate exceptional solvent resistance and mechanical durability. Most preferably, they are also fabricated from polyolefin materials.

As admitted by the Examiner, Huang does not teach a method in which the potting material and the hollow fibers both consist of all thermoplastic perfluorinated resin materials. For these modifications of the Huang invention, the Examiner relies upon two secondary references, EP 0299459 A2 and Miyagi (US 5,114,508). This proposed combination of references is respectfully traversed for the following reasons:

The Federal Circuit states that " [t]he mere fact that the prior <u>may be</u> modified in the manner suggested by the Examiner does not make the modification obvious unless the prior art suggested the desirability of the modification." *In re Fritch*, 972 F.2d 1260, 1266 n.14, 23 USPQ 1780, 1783-84 n.14 (Fed. Cir. 1992) (citing *In re Gordon*, 733 F.2d 900, 902, 221 USPQ 1125, 1127 (Fed. Cir. 1984)). It is further established that "[s]uch suggestion may come from the nature of the problem to be solved, leading inventors to

look to references relating to possible solutions to that problem." *Pro-mold & Tool Co. v. Great Lakes Plastics, Inc.*, 75 F. 3d 1568, 1573, 37 USPQ2d 1626, 1630 (Fed. Cir. 1996) (citing *In re Rinehart*, 531 F.2d 1048, 104, 189 USPQ 143, 149 (CCPA 1976) (considering the problem to be solved in a determination of obviousness)). The Federal Circuit reasons in *Para-Ordnance Mfg. Inc. v. SGS Importers Int'l Inc.*, 73 F. 3d 1085, 1088-89, 37 USPQ2d 1237, 1239-40 (Fed. Cir. 1995), *cert. denied* 519 U.S. 822 (1966), that for the determination of obviousness, the court must answer whether one of ordinary skill in the art who sets out to solve the problem and who had before him in his workshop the prior art, would have been reasonable expected to use the solution that is claimed by the Applicants. However, "[o]bviousness may not be established using hindsight or in view of the teachings or suggestions of the invention." *Para-Ordinance Mfg. V. SGS Importers Int'l*, 73 F.3d at 1087, 37 USPQ at 1239, citing *W.L. Gore & Assoc., Inc. v. Garlock, Inc.*, 721 F.2d at 1551, 1553, 220 USPQ at 311, 312-13.

In addition, the Federal Circuit requires the PTO to make specific findings on a suggestion to combine prior art references. *In re Dembiczak*, 175 F.3d 994, 1000-01, 50 USPQ2d 1614, 1617-19 (Fed. Cir. 1999). Here, that has not been done. Where is the motivation in Huang to change from polyolefin materials to perfluorinated materials?

When references are proposed to be combined, they must first be considered for all that they teach, not selected portions of the teachings. Both the EP Patent (as previously discussed above) and Miyagi teach very different processes that that taught by Huang. Accordingly there is no way to be sure that the materials used in these different processes would be compatable with the process used by Huang for his polyolefin materials. While it might be "obvious to try" these materials, that is not a propser basis for a Section 103 rejection.

The Examiner's position is that it would be obvious to one of ordinary skill in the art at the time of invention to use the teaching of EP and Miyagi in the process of Huang to obtain hollow fiber modules with "excellent heat and chemical resistance" as taught by EP and Miyagi. Why? Huang already obtains such a result using his preferred polyolefin materials. Why would he change to the materials used in completely different processes as taught in EP and Miyagi? No reason is given, and accordingly the Section 103 rejection combining these three references is not supported, and must be withdrawn. Such action is respectfully requested.

PETITION FOR EXTENSION OF TIME

Applicant hereby petitions for a two-month extension of time for the filing of this response. The initial response deadline was July 12, 2004. A two-month extension of time moves that date to September 13, 2004 (the 12th being a Sunday).

FEE AUTHORIZATION

Please charge all fees (extra claims, time extension, etc.) due in connection with this filing to Deposit Account No. 19-0733.

CERTIFICATE OF FACSIMILE TRANSMISSION

The undersigned hereby certifies that this correspondence was submitted by facsimile in the USPTO on the date shown on Page 1.

Respectfully submitted,

Ernest V. Linek (29,822)
Attorney for Applicant

Document No. 100515

Summary of the Invention

This Invention provides for the first time for an asymmetric hollow fiber porous membranes, skinned on at least one surface, more specifically, ultrafiltration and contactor membranes, from perfluorinated thermoplastic polymers, more specifically poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) (poly(PTFE-CO-PFVAE)) or poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP). These membranes are capable of operating in severe chemical environments with no apparent extractable matter being released. These membranes have low surface tension properties, which allows them to be used as contactors with fluids having surface tension lower than water.

A process to produce these membranes is provided. The process is based on the Thermally Induced Phase Separation (TIPS) method of making porous structures and membranes. A mixture of polymer pellets, usually ground to a size smaller than supplied by the manufacturer, to about 100 to about 1000 micron size, preferably to about 300 microns, and an solvent, such as chlorotrifluoroethylene oligimer, is first mixed to a paste or paste-like consistency. The polymer comprises between approximately 12% to 75%, preferably 30% to 60%, by weight of the mixture. The solvent is chosen so the membrane formation occurs by liquid-liquid, rather than solid-liquid phase separation when the solution is extruded and cooled. Preferred solvents are saturated low molecular weight polymers of chlorotrifluoroethylene. A preferred solvent is HaloVac® 60 from Halocarbon Products Corporation, River Edge, NJ. Choice of the solvent is dictated by the ability of the solvent to dissolve the polymer when heated to form an upper critical solution temperature solution, but not to excessively boil at that temperature. Fiber extrusion is referred to as spinning and the extruded fiber length from the die exit to the take-up station is referred to as the spin line. The paste is metered into a heated extruder barrel where the temperature raised to above the upper critical solution temperature so that dissolution occurs. The homogeneous solution is then extruded through an annular die directly into a liquid cooling bath with no air gap. The liquid cooling bath is maintained at a temperature below the upper critical solution temperature of the polymer solution. The preferred bath liquid is not a solvent for the thermoplastic polymer, even at the extrusion temperature. Upon cooling, the heated and shaped solution undergoes phase separation and a gel fiber results. The die tip is slightly submerged for vertical spinning, i.e., the spin line falls downward, in the direction of a freely falling body. For horizontal spinning, where the spin line exits directly in the horizontal attitude, and is maintained more or less in that plane until at least the first guide roll, a specially design die is

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used. The die is firmly positioned against an insulated wall with the die tip penetrating through a opening having a liquid-tight seal in the insulator wall. A trough for cooling liquid flow is placed in a recess in the opposite side of the insulating wall, in a manner that will maintain the die nose outlet in a submerged condition. Cooling liquid flows in the trough and overflows in a region of the trough of lesser depth, keeping the die nose outlet submerged with a flow of cooling liquid. In both the vertical and horizontal methods, a booster heater and temperature control means is used to briefly raise the solution temperature at the die tip to prevent premature cooling. In a subsequent step, the dissolution solvent is removed by extraction and the resultant hollow fiber membrane is dried under restraint to prevent membrane shrinkage and collapse. Optionally the dried fiber may be heat set at 200°C to 300°C.

US Patent Application MCA 389, our number, serial number not yet assigned, filed concurrently, the disclosure of which is incorporated by reference, describes a process for manufacturing hollow fiber microporous membranes using a submerged die tip to prevent solvent from flashing off from the outer diameter. Flashing caused an increase in the polymer content at that surface and a dense skin to form. This was deleterious to microporous membrane properties. In that process, polymer solutions of from about 12% to about 35% were used in the membrane making process. It was found that at solutions of higher than about 35%, the porosity was too low to produce a useful microporous membrane. Also, in that process, a liquid was co-extruded in the lumen of membrane while the hollow fiber microporous membrane was extruded. This lumen fluid was necessary to control the porosity of the hollow fiber membrane by preventing solvent from flashing from the extrudate surface and thereby increasing the polymer concentration at the surface and subsequent skin formation.

In the present invention, controlled evaporation of solvent from at least one surface of the hollow fiber as it exits the die tip is combined with higher polymer solids solutions and the submerged extrusion process to produce asymmetric hollow fiber porous membranes, skinned on at least one surface, more specifically, ultrafiltration and contactor membranes, from perfluorinated thermoplastic polymers. It was found that polymer concentrations required to make suitable membranes for the purposes described were from about 12% to about 75%, with preferred concentrations from about 30% to about 60%. Furthermore, the lumen liquid was replace with a fluid, preferably a gas, that does not prevent solvent evaporation. Without the presence of the lumen liquid of the above invention, the superheated solvent evaporates inside the lumen as soon as it emerges from the die. The loss of solvent causes a superficial

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quenching of the surfaces. Third, the hot oil tends to soften the extruded melt and the extruded fiber tends to break apart during processing.

Post-stretching was disclosed as another technique to enhance permeability of a skinned PFA membrane in US Patents 4,990,294, and 5,032,274. While stretching does increase permeability substantially, it produces its own set of undesirable side-effects. First, for stretching to be effective, the base skinned membrane must be very uniform in thickness and in mechanical strength. Any non-uniformity in the base membrane will be amplified as soon as the membrane is subjected to stretching, because weak areas stretch more than strong areas under the same stretching force. As mentioned above, it is very difficult to produce base membranes with the solvent coating technique. If solvent coating is not used, the heavy evaporation of porogen usually produces dried polymer on the die lips. This accumulated dried polymers then scratch the melt surfaces, producing lines of hidden weaknesses in the base membrane. Upon stretching, the weakened membranes would break apart along the "scratch" lines.

It would therefore be desirable to have a process that would eliminate the rapid evaporation of solvent from the fiber surface, but not require a difficult coating or stretching step. It would also be beneficial to produce a skinless membrane having high surface porosity in order to utilize a large proportion of the membrane surface for permeation and retention.

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Summary of the Invention

This Invention provides for high flux, skin-free hollow fiber porous membranes, more specifically, microporous membranes, from perfluorinated thermoplastic polymers, more specifically poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) (POLY(PTFE-CO-PFVAE)) or poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP). These membranes are capable of operating in severe chemical environments with no apparent extractable matter being released. Compared to prior art membranes, the membranes of the invention have a higher surface porosity, which translates into high permeability or flux.

A process to produce these membranes is provided. The process is based on the Thermally Induced Phase Separation (TIPS) method of making porous

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structures and membranes. A mixture of polymer pellets, usually ground to a size smaller than supplied by the manufacturer, and an solvent, such as chlorotrifluoroethylene oliglmer, is first mixed to a paste or paste-like consistency. The polymer comprises between approximately 12% to 35% by weight of the mixture. The solvent is chosen so the membrane formation occurs by liquid-liquid, rather than solid-liquid phase separation when the solution is extruded and cooled. Preferred solvents are saturated low molecular weight polymers of chlorotrifluoroethylene. A preferred solvent Is HaloVac® 60 from Halocarbon Products Corporation, River edge, NJ. Choice of the solvent is dictated by the ability of the solvent to dissolve the polymer when heated to form an upper critical solution temperature solution, but not to excessively boil at that temperature. Fiber extrusion Is referred to as spinning and the extruded fiber length from the die exit to the take-up station is referred to as the spin line. The paste Is metered into a heated extruder barrel where the temperature raised to above the upper critical solution temperature so that dissolution occurs. The homogeneous solution is then extruded through an annular die directly into a liquid cooling bath with no air gap. The liquid cooling bath is maintained at a temperature below the upper critical solution temperature of the polymer solution. The preferred bath liquid is not a solvent for the thermoplastic polymer, even at the extrusion temperature. Upon cooling, the heated and shaped solution undergoes phase separation and a gel fiber results. The die tip is slightly submerged for vertical spinning, i.e., the spin line falls downward, in the direction of a freely falling body. For horizontal spinning, where the spin line exits directly in the horizontal attitude, and is maintained more or less in that plane until at least the first guide roll, a specially design die is used. The die is firmly positioned against an insulated wall with the die tip penetrating through a opening having a liquid-tight seal in the insulator wall. A trough for cooling liquid flow is placed in a recess in the opposite side of the insulating wall, in a manner that will maintain the die nose outlet in a submerged condition. Cooling liquid flows in the trough and overflows in a region of the trough of lesser depth, keeping the die nose outlet submerged with a flow of cooling liquid. In both the vertical and horizontal methods, a booster heater and temperature control means is used to briefly raise the solution temperature at the die tip to prevent premature cooling. In a subsequent step, the dissolution

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solvent is removed by extraction and the resultant hollow fiber membrane is dried under restraint to prevent membrane shrinkage and collapse. Optionally the dried fiber may be heat set at 200°C to 300°C.

Brief Description of the Drawings

Figure 1 is a flow diagram of the process of this invention with vertical extrusion.

Figure 2 is a flow diagram of the process of this invention with horizontal extrusion.

Figure 3 is a drawing of the die used in vertical fiber spinning.

Figure 4 is a drawing of the die used in horizontal fiber spinning.

Figure 5 is a photomicrograph at 3191X of the inner surface of a hollow fiber microporous membrane made from poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) made in accordance with Example 1, Sample #3.

Figure 6 is a photomicrograph at 3191X of the outer surface of a hollow fiber microporous membrane made from poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) made in accordance with Example 1, Sample #3.

Figure 7 is e photomicrograph at 3395X of the inner surface of a hollow fiber microporous membrane made from poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) made in accordance with Example 1, Sample #8.

Figure 8 is a photomicrograph at 3372X of the outer surface of a hollow fiber microporous membrane made from poly(tetrafluoroethylene-co-perfluoro(alkylvinylether)) made in accordance with Example 1, Sample #8.

Figure 9 is a photomicrograph at 984X of the inner surface of a hollow fiber microporous membrane made from poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), made in accordance with Example 5.

Figure 10 is a photomicrograph at 1611X of the outer surface of a hollow fiber microporous membrane made from poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), made in accordance with Example 5.

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